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Midlatitude ClO during the maximum atmospheric chlorine burden: in situ balloon measurements and model simulations

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Abstract. Chlorine monoxide (ClO) plays a key role in stratospheric ozone loss processes at midlatitudes. We present two balloon-borne in situ measurements of ClO conducted in northern hemisphere midlatitudes during the period of the maximum of total inorganic chlorine loading in the atmosphere. Both ClO measurements were conducted on board the TRIPLE balloon payload, launched in November 1996 in León, Spain, and in May 1999 in Aire sur l'Adour, France. For both flights a ClO daylight and night-time vertical profile was derived over an altitude range of approximately 15–35 km. ClO mixing ratios are compared to model simulations performed with the photochemical box model version of the Chemical Lagrangian Model of the Stratosphere (CLaMS). Simulations along 24-hour backward trajectories were performed to study the diurnal variation of ClO in the midlatitude lower stratosphere. Model simulations for the flight launched in Aire sur l'Adour 1999 show an excellent agreement with the ClO measurements. For the flight launched in León 1996, an overall good agreement is found, whereas the flight is characterized by a more complex dynamical situation due to a possible mixture of vortex and non-vortex air. We note that for both flights at solar zenith angles greater than 86°–87° simulated ClO mixing ratios are higher than observed ClO mixing ratios. However, the present findings indicate that no substantial uncertainties exist in midlatitude chlorine chemistry of the stratosphere.

1 Introduction

Stratospheric ozone has globally decreased over the last ≈ 25 years. In midlatitudes, the vertical, latitudinal, and seasonal characteristics of changes in ozone are broadly consistent with the understanding that halogens are the primary cause of these changes (WMO, 2003). A downward ozone trend of -1 to -3% per decade is estimated for the lower stratosphere in the northern and southern hemisphere midlatitudes for the time period between 1979 and 2000 (Wang et al., 2002; WMO, 2003). Furthermore, it was found that the large ozone depletions determined for the Arctic vortex in several previous winters will ultimately spread out and dilute ozone concentrations at midlatitudes thereby contributing to the observed ozone decrease at midlatitudes (e.g., Chipperfield, 1999; Knudsen and Grooß, 2000; Marchand et al., 2004). The catalytic loss of ozone in the lower stratosphere is controlled by a combination of cycles involving reactions with BrO, ClO, HO₂, and NO₂ (e.g., Wennberg et al., 1994; Stimpfle et al., 1994). Thus a prerequisite for a reliable calculation of halogen-induced ozone loss rates at midlatitudes is information about ClO concentrations at midlatitudes and an understanding of the dependence of ClO concentrations on altitude and time of day.

Nonetheless, measurements of ClO at midlatitudes in the lower stratosphere are rare. Early balloon-borne in situ (e.g., Anderson et al., 1977; Anderson, 1978; Anderson et al., 1980) and remote (Menzies, 1979) measurements of ClO were made in the late 1970s and 1980s all launched from Palestine (32° N), Texas. In the 1990s, balloon-borne in situ measurements (e.g., Toohey et al., 1993a) and remote measurements (e.g., Osterman et al., 1997) of ClO were obtained at somewhat higher latitudes (launched from Fort Sumner (34.5° N), New Mexico). In situ measurements of ClO conducted on board the ER-2 aircraft cover a greater

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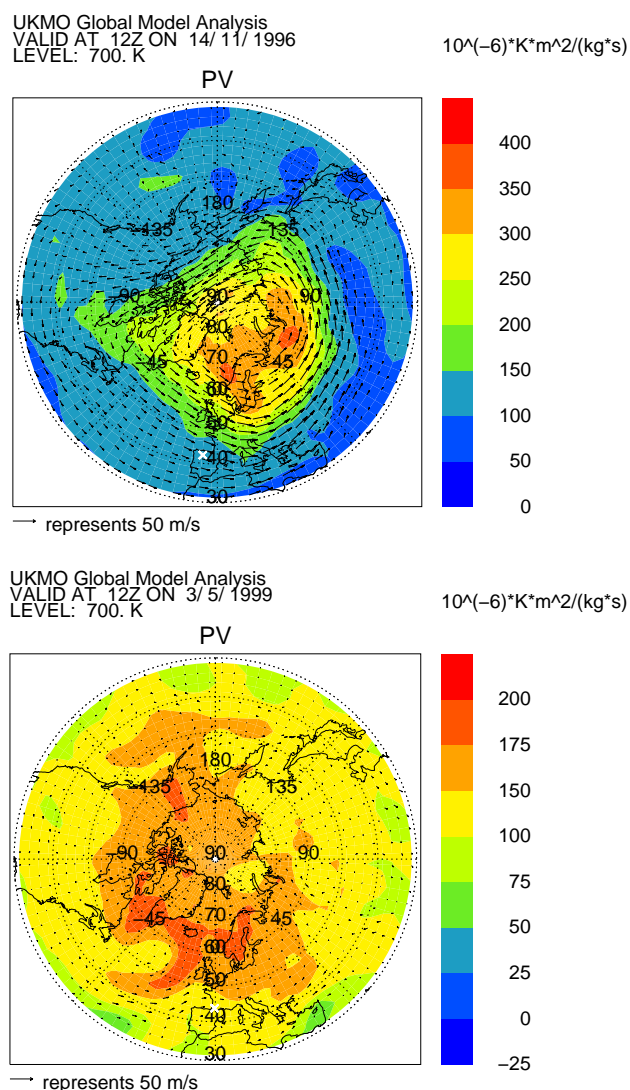


Fig. 1. Potential vorticity ($1 \text{ PVU} = 10^{-6} \text{ K m}^2 \text{ kg}^{-1} \text{ s}^{-1}$) on 14 November 1996 (top panel) and on 3 May 1999 (bottom panel), 12.00 UT on the 700 K isentropic level derived from data of the UK Met Office (UKMO) analyses. The wind direction is marked by arrows whose length is proportional to horizontal wind velocity. The location where the balloon was launched (León, Spain (top panel), and Aire sur l'Adour, France (bottom panel)) is marked by a white cross.

range of the midlatitudes (e.g., Stimpfle et al., 1999; Toohey et al., 1991; King et al., 1991; Toohey et al., 1993b), but only a rather small altitude range of ≈ 16 – 20 km. Global or near global measurements of ClO are available from the Microwave Limb Sounder (MLS) aboard the Upper Atmosphere Research Satellite (UARS) (e.g., Ricaud et al., 2000) and the Millimeter-wave Atmospheric Sounder (MAS) from three space shuttle missions in 1992, 1993, and 1994 (e.g., Feist et al., 2000). The analysis of ClO measurements from the recently launched MIPAS-E and ODIN instruments has

focussed on the polar regions so far (e.g., Glatthor et al., 2004; Urban et al., 2004). In summary, at midlatitudes ($\approx 35^\circ \text{ N}$ – 60° N), in situ as well as remote measurements of ClO over the entire altitude range of the lower stratosphere (≈ 15 – 30 km) are very sparse.

As a result of the Montreal Protocol and its amendments and adjustments, in 1997–1998 the total inorganic chlorine stopped increasing in the troposphere and has remained fairly constant since that time. That is to say the loading of inorganic chlorine Cl_y in the unperturbed stratosphere has recently stabilized (WMO, 2003). Here we present the only two balloon-borne in situ measurements of ClO performed in the lower stratosphere at midlatitudes during the period of the maximum of total inorganic chlorine loading in the atmosphere. Furthermore, after the eruption of Mount Pinatubo (June 1991) and the dissipation of the post-Pinatubo aerosol the aerosol levels were low from 1996 to 1999 (e.g., Bauman et al., 2003) with simultaneously the maximum atmospheric chlorine burden. The two ClO in situ measurements were conducted on board the TRIPLE balloon payload launched in November 1996 in León (42.3° N), Spain, and in May 1999 in Aire sur l'Adour (43.7° N), France. Both flights were optimized in such a way that both a vertical ClO daylight and night-time profile could be measured over an altitude range of approximately 15–35 km.

Further, photochemical model studies were performed using the box model version of the Chemical Lagrangian Model of the Stratosphere (CLaMS) (McKenna et al., 2002a,b) to test whether model simulations can reproduce the diurnal behavior of ClO at midlatitudes over the entire range of the lower stratosphere. In previous photochemical model studies for midlatitude conditions based on ER-2 measurements, the ClO photochemistry was described correctly by the models (e.g., Brune et al., 1990; Salawitch et al., 1994; Stimpfle et al., 1994). However, discrepancies in the understanding of the chlorine budget remained unresolved at that time (e.g., Stimpfle et al., 1994). In a more recent study, Sen et al. (1999) obtained a good understanding of the budget of stratospheric chlorine using balloon-borne measurements and found that the partitioning of inorganic chlorine is accurately described by photochemical models employing reaction rates recommended by DeMore et al. (1997). In a model study based on balloon-borne in situ measurements of ClO (Avalone et al., 1993), observed ClO was greater by as much as a factor of four below 20 km altitude. Studies on the broadband photolysis of ClONO_2 led to the speculation that there is a pressure dependence of the ClONO_2 quantum yield beyond 300 nm (Nickolaisen et al., 1996), but first in situ measurements of ClONO_2 on board the ER-2 aircraft during the northern high-latitude summer found no evidence in support of a pressure-dependent quantum yield for photodissociation of ClONO_2 (Stimpfle et al., 1999). Further, no evidence was found from these ER-2 measurements in support of missing inorganic chlorine species that would constitute a significant fraction of Cl_y (Bonne et al., 2000).

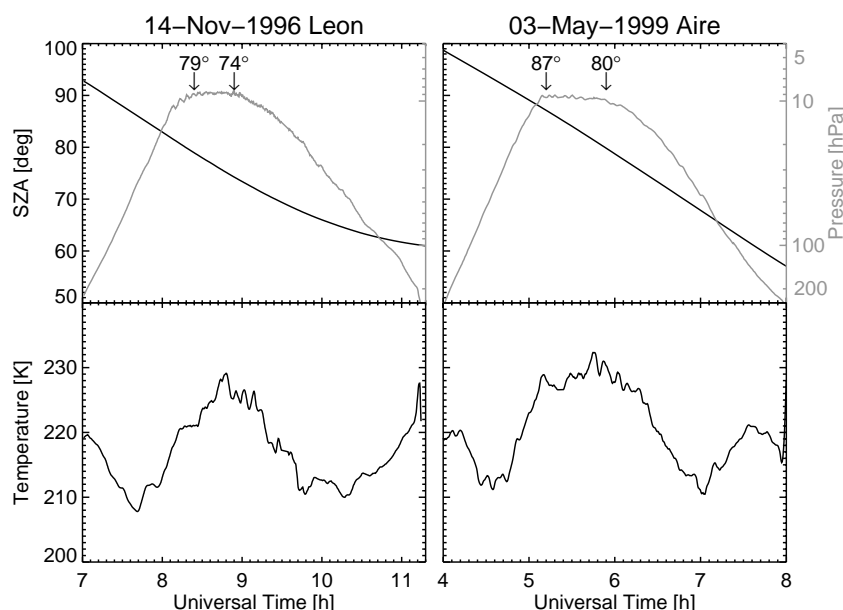


Fig. 2. Meteorological parameters for the flights of the TRIPLE payload on 14 November 1996 (left) and on 3 May 1999 (right) as a function of UT time. Top panel: pressure (gray line) and solar zenith angle (SZA) (black line). Beginning and end of the float is marked by arrows; the corresponding solar zenith angles are also noted. Bottom panel: temperature (black line).

2 Observations

The ClO measurements were conducted on board the balloon-borne multi-instrument payload TRIPLE launched on 14 November 1996 from León (42.3° N, 5.4° W), Spain, and on 3 May 1999 from the French launching base in Aire sur l'Adour (43.7° N, 0.3° W), France (in the following referred to as León and Aire flights). TRIPLE consists of the Jülich ClO/BrO in situ instrument (Vogel et al., 2003), the cryogenic whole air sampler of the University of Frankfurt (Schmidt et al., 1987) for the observation of long-lived tracers and various CFCs, from which the amount of total inorganic chlorine, Cl_y , can be inferred (Schmidt et al., 1994; Engel et al., 1997), and the Jülich Fast In Situ Stratospheric Hygrometer (FISH) (Schiller et al., 2002).

On 14 November 1996, a prototype of the Jülich ClO/BrO in situ instrument (Pierson et al., 1999; Woyke et al., 1999) was flown, whereas on 3 May 1999 the new Jülich ClO/BrO in situ instrument (Vogel et al., 2003) was part of the payload. Both instruments employ the well-established chemical-conversion resonance-fluorescence technique (Brune et al., 1989).

2.1 Meteorological Situation

The dynamical situation of the stratosphere was very different for the two balloon flights. The flight in November 1996 was conducted during the typical time period of the formation of the Arctic polar vortex in the northern hemisphere,

whereas the flight in May 1999 took place after the dissipation of the polar vortex in spring (see Fig. 1).

The meteorological analysis by FU Berlin for the flight in November 1996 shows that in October 1996 the Arctic polar vortex was more strongly developed than normal. In early November the vortex was split and the center of the vortex was displaced out of the pole towards Greenland. From 7 November, the center of the vortex moved eastward, which caused a temperature decrease and an increase in potential vorticity over Northern Spain until 11 November. Afterwards, the wind speed decreased over Northern Spain, because the center of the vortex moved further on eastwards. On 14 November 1996, León was located outside the polar vortex. The air masses probed on this day had previously been led around the Atlantic anticyclone and had crossed the cold area over Iceland in the lower stratosphere.

The flight in May 1999 occurred after a Northern winter with a perturbed weak polar vortex. Through most of the Arctic winter 1998/1999, the polar vortex was unusually warm and weak due to an atypically early major stratospheric sudden warming occurring in mid-December. A second major warming followed in late February (Manney et al., 1999). As a consequence, the vortex was strongly eroded at the time of the flight as is obvious from Fig. 1.

2.2 Flight Profiles

For both balloon flights a flight profile was employed to study in detail the sunrise evolution of the ClO mixing ratios (see Fig. 2).

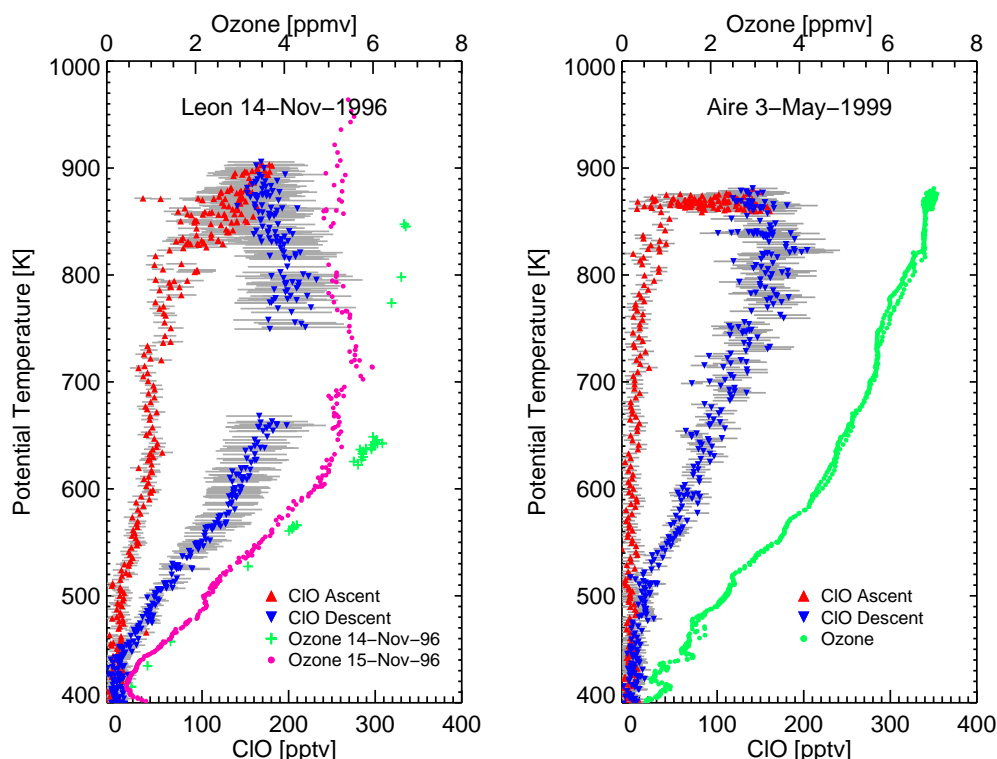


Fig. 3. Measured ClO mixing ratios as a function of the potential temperature of the balloon flights launched on 14 November 1996 in León (left) and on 3 May 1999 in Aire sur l'Adour (right). The 1σ accuracy for the ClO measurements is approximately 20–23% (gray bars). For the 1996 flight, no data could be obtained at around 720 K due to a temporary malfunction of the photomultiplier. In addition, for both flights O_3 mixing ratios are shown measured simultaneously by an ECC ozone sonde on board the TRIPLE payload. Because the signal of the ozone sonde was jammed on 14 November 1996, additional ozone measurements are shown which were made by an ozone sonde launched in León on 15 November 1996.

On 14 November 1996, the TRIPLE payload was launched at approximately 6.30 UT. After reaching a maximum altitude of approximately 35 km (≈ 9 hPa), a balloon float took place in the 79° – 74° solar zenith angle (SZA) interval. During descent SZAs between 74° and 63° were encountered.

On 3 May 1999, the TRIPLE payload was launched at approximately 3.30 UT. The entire balloon ascent was conducted at night (SZA $> 87^\circ$). After reaching a maximum altitude of approximately 31 km (≈ 9 hPa), the balloon floated at this altitude between 87° and 80° SZA into the sunrise, so that within this air mass the increase of the ClO mixing ratios could be measured. During descent a ClO daylight profile was measured between 80° and 65° SZA.

2.3 ClO and O_3 Measurements

The ClO vertical profiles measured by the TRIPLE balloon payload on 14 November 1996 and on 3 May 1999 are shown in Fig. 3.

On 14 November 1996, a ClO profile was measured during ascent with ClO mixing ratios of up to 150 pptv at float altitude. During descent a ClO daylight profile was measured with ClO peak values of approximately 220 pptv be-

tween 750 and 800 K potential temperature. In Fig. 3 (left panel), ozone mixing ratios are shown which were measured simultaneously by an ECC (electrochemical concentration cell) ozone sonde on board TRIPLE. The signal of the ozone sonde was jammed, so ozone measurements could not be obtained for all altitudes. Therefore in Fig. 3 (left panel) in addition, an ozone profile is shown measured by an ozone sonde launched in León one day after the balloon flight on 15 November 1996. Above 650 K potential temperature, the ozone measurements on 15 November are much lower than on 14 November 1996.

The balloon ascent on 3 May 1999, was during the night so that very low ClO mixing ratios, lower than 50 pptv, were measured (see Fig. 3, right panel). On the float level, ClO mixing ratios increase during sunrise up to approximately 130 pptv. For the ClO daylight profile measured during descent, maximum ClO mixing ratios of approximately 200 pptv were obtained at around 840 K potential temperature. Additionally in Fig. 3 (right panel), an ozone profile simultaneously measured by an ECC ozone sonde on board TRIPLE is shown.

For both flights, the overall accuracy of the ClO measurement is ≈ 20 – 23% . For measured ClO mixing ratios below 50 pptv we deduced an error of ± 10 pptv.

We compared the measured ClO mixing ratios at around 22 hPa from both balloon flights with the seasonal variation of lower stratospheric ClO mixing ratios in the northern hemisphere midlatitudes derived from MLS measurements for the time period between September 1991 and December 1993 (Fig. 4–7, WMO, 1995). While a direct comparison of absolute ClO values is difficult due to the slight increase in chlorine loading and differences in solar zenith angles, it seems that the differences in the ClO abundances measured by balloons at 22 hPa (≈ 650 K) in November and May corroborate the seasonal variation in MLS observations at similar altitudes. Further examination of this feature would be worthwhile.

3 Model Simulations

Model simulations were performed to investigate whether the measured diurnal variation of chlorine monoxide can be reproduced at midlatitudes over the altitude range between 20 and 35 km. ClO mixing ratios measured at one particular level of potential temperature during ascent and descent yield two points within the diurnal variation of ClO. Therefore differences in ClO mixing ratios between ascent and descent can be used to test our understanding of the photochemical evolution of ClO during sunrise, similar to the model study by Pierson et al. (1999) performed for activated conditions. Here we use the **C**hemical **L**agrangian **M**odel of the **S**tratosphere (CLaMS) (McKenna et al., 2002a,b). This model simulates both the chemistry of multiple air parcels and their transport and is used here as a photochemical box model. The absorption cross sections and reaction rate constants are taken from standard recommendations (Sander et al., 2002). For simulations with the CLaMS model, the family concept (IMPACT) is usually employed as the integration solver (McKenna et al., 2002b). In all model simulations presented in this work, the explicit stiff solver SVODE (McKenna et al., 2002b) is used which is more precise but numerically more expensive. As input data for the photolysis scheme an ozone profile is derived from model results of the Mainz 2-D model (Gidel et al., 1983; Groö, 1996) below 15 km altitude and from observations of the Halogen Occultation Experiment (HALOE) on board the UARS satellite (Russell et al., 1993) above 15 km altitude. The surface area of the background aerosol ($SSA = \text{stratospheric sulfu-ric aerosol}$) per unit volume A_{SSA} was adjusted by varying the mixing ratio of H_2SO_4 in ppbv in the gas-phase equivalent employing a stratospheric aerosol climatology based on SAGE II and CLAES measurements by Bauman et al. (2003).

We performed simulations along 24-hour backward trajectories calculated from the locations of the measurements

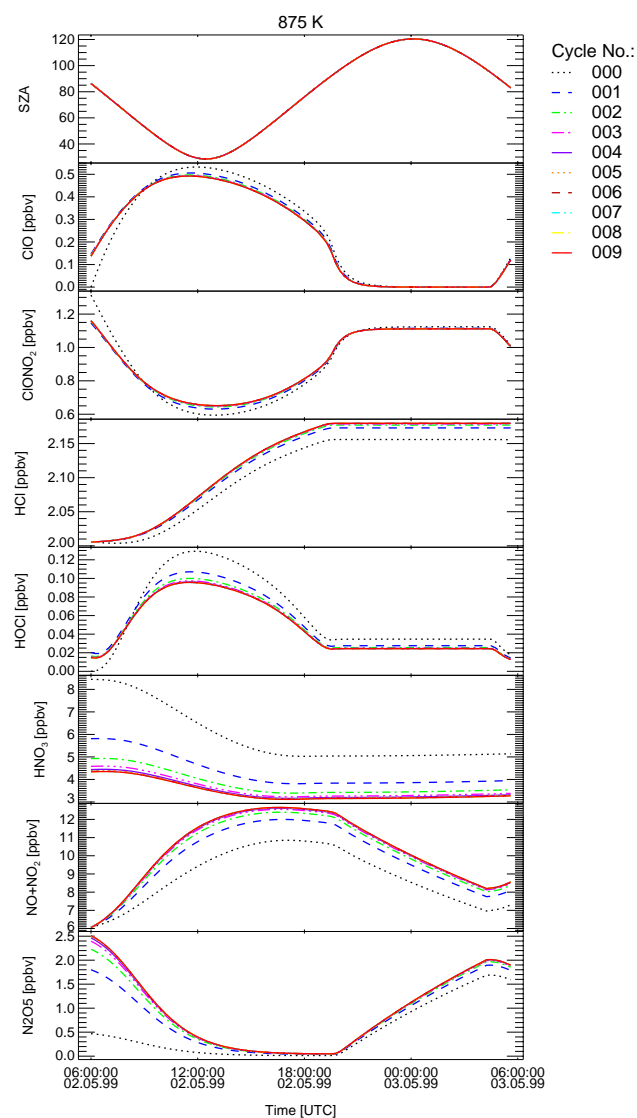


Fig. 4. The convergence of the simulated diurnal variation of various species for cycles 0 to 9 is shown at 875 K potential temperature for the flight launched on 3 May 1999 in Aire sur l'Adour.

starting at different levels of potential temperature between 500 K and the float altitude (≈ 865 K– 900 K) and for different SZAs during float (see Figs. 6 and 8). We calculated these backward trajectories using wind data from the UK Met Office (UKMO) analyses. A chemical initialization had to be determined for the simulations at each level of potential temperature. All available stratospheric measurements, together with tracer-tracer correlations, and model simulations, were used as sources for this initialization. Table 1 gives an overview over the measurements employed in order to derive the initialization of the most important species for the model simulations. We calculate the temporal development of the chemical trace species along each 24-hour backward trajectory continually using the results of the previous

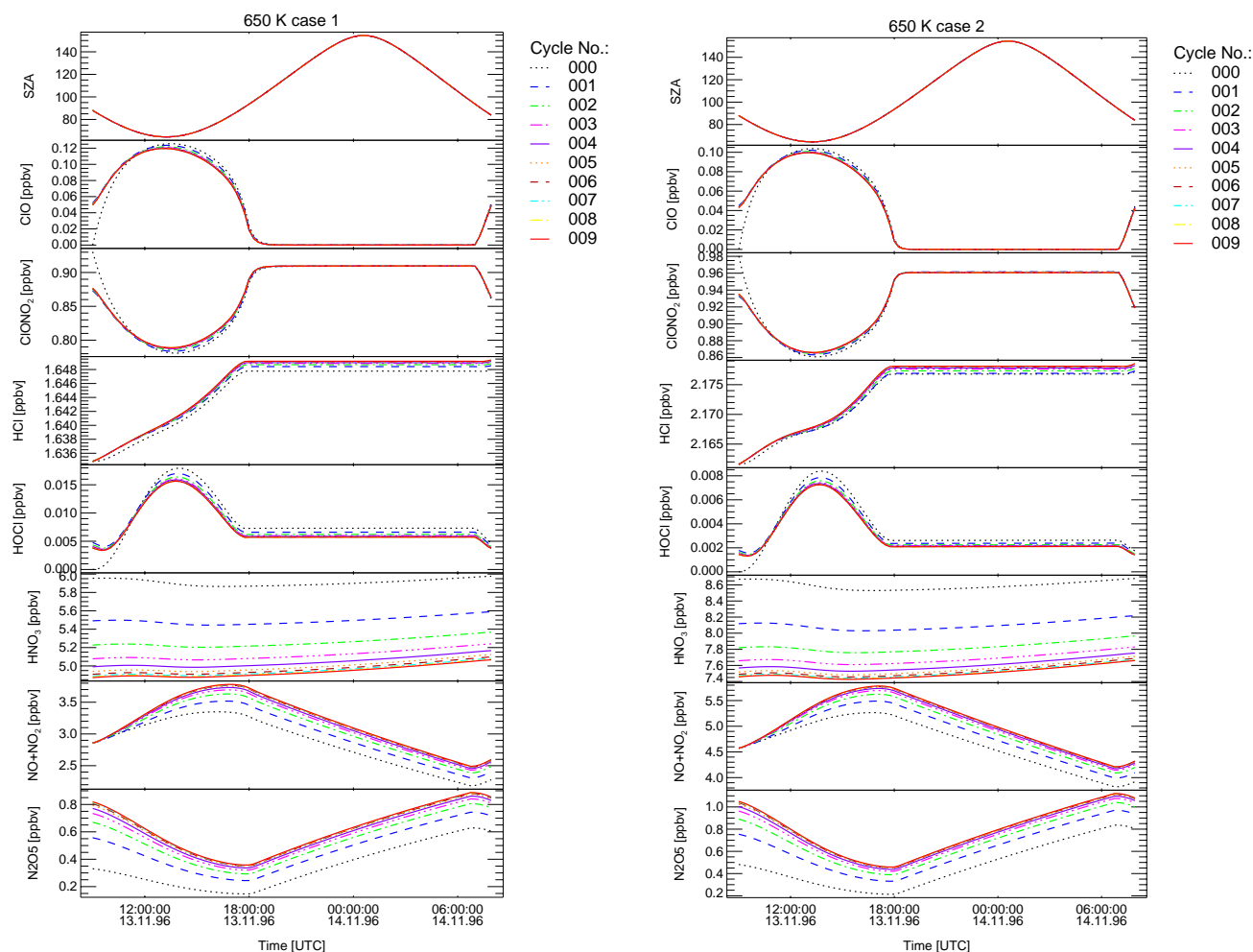


Fig. 5. The convergence of the simulated diurnal variation of various species for cycles 0 to 9 is shown at 650 K potential temperature for the flight launched on 14 November 1996 in León.

model simulation to initialize the following 24-hour simulation, whereas the species CH_4 , HCl , H_2O , NO_x , and O_3 derived from measurements are reinitialized to measured values. The conservation of Br_y , Cl_y , and NO_y is guaranteed between the different cycles.

After approximately 6–9 cycles, depending on altitude, most chemical species converge to a constant volume mixing ratio for a given time in the simulation (see Figs. 4 and 5). Additionally, model simulations using different initializations for the partitioning between HNO_3 and N_2O_5 (cf. Table 1) converge to the same ClO mixing ratios after approximately 9 cycles. The volume mixing ratios of the important species used to initialize the model simulations for the last cycle are shown in Tables 2, 3, and 4.

3.1 Results for the Flight on 3 May 1999

Figure 6 shows that the simulated ClO mixing ratios agree excellently with the ClO measurements. We note that for the night-time ClO profile ($\text{SZA} > 87^\circ$) the model simulations are at the upper limit of the measurements. A possible deviation of simulated ClO mixing ratios from measured ClO mixing ratios depending on solar zenith angle is discussed in Sect. 3.3. The simulated diurnal variation of ClO and various other species are shown for different levels of potential temperature in Fig. 7. The sensitivity of the model simulations toward the surface area of the background aerosol per unit volume A_{SSA} was examined. Simulations with A_{SSA} values significantly higher and lower than reported by Bauman et al. (2003) were performed (cf. Table 5). However, the sensitivity of ClO mixing ratios on the surface area of the background aerosol is not substantial ($< 3\%$).

Table 1. Sources of the major chemical species used to initialize the model simulations for the flight on 5 May 1999 launched in Aire sur l'Adour and for the flight on 14 November 1996 launched in León.

Species	Aire sur l'Adour 1999	León 1996
CH ₄	cryogenic whole air sampler ^a	HALOE (1–5 Nov. and 15–22 Nov. 1996) ^f
N ₂ O	cryogenic whole air sampler ^a	CH ₄ –N ₂ O correlation ^g
Cl _y	cryogenic whole air sampler ^a	N ₂ O–Cl _y correlation ^h
HCl	HALOE (25–27 April 1999) ^b	HALOE ^f
ClONO ₂	Cl _y –HCl	Cl _y –HCl
ClO	as zero ^c	as zero ^c
NO _y	N ₂ O–NO _y correlation ^d	N ₂ O–NO _y correlation ^d
NO _x =NO+NO ₂	HALOE ^b	HALOE ^f
HNO ₃ +2×N ₂ O ₅	=NO _y –ClONO ₂ –NO _x ^e	=NO _y –ClONO ₂ –NO _x ^e
O ₃	ozone sonde ^a	HALOE ^f
H ₂ O	HALOE ^b	HALOE ^f
all other	Mainz 2-D model	Mainz 2-D model (Gidel et al., 1983; Grooß, 1996)

^a Conducted on board TRIPLE (cf. Sect. 2)

^b Observations of the Halogen Occultation Experiment (HALOE) on board the UARS satellite (Russell et al., 1993) in northern hemisphere midlatitudes (within 35° N and 50° N) are only available between 25 and 27 April 1999. A mean vertical profile is derived.

^c ClO and all other chlorine species, except ClONO₂ and HCl were initialized as zero.

^d This correlation (Sugita et al., 1998) was derived from measurements by the ATMOS (*Atmospheric Trace Molecule Spectroscopy*) instrument on board the space shuttle during the ATLAS 3 mission within a period of 10 days in early November 1994. The correlation is valid for high and midlatitudes.

^e As upper and lower limits for the partitioning, we assume a ratio of HNO₃:2×N₂O₅ of 9:1 and of 1:9, respectively. All other species of the nitrogen family were initialized as zero.

^f A mean profile derived from HALOE measurements between 1–5 November and 15–22 November 1996 within 35° N and 50° N for midlatitude (case 1) and vortex (case 2) air masses (cf. Sect. 3.2)

^g A CH₄–N₂O correlation is used derived from measurements of the ATMOS instrument conducted during different missions in March 1992, April 1993, and November 1994 (Michelsen et al., 1998) for midlatitudes (case 1). For vortex conditions (case 2), we employed the CH₄–N₂O correlation (Grooß et al., 2002) to determine N₂O derived from measurements conducted on board the ER-2 aircraft and on board the TRIPLE payload during the Arctic winter 1999/2000 inside the vortex. Above 25 km altitude (the maximum altitude of the TRIPLE flights), a CH₄–N₂O correlation is used derived from ATMOS measurements for polar latitudes (Michelsen et al., 1998)

^h To infer Cl_y, we used for midlatitude and vortex conditions the N₂O–Cl_y correlation derived from measurements of the cryogenic whole air sample on board the TRIPLE payload conducted in Kiruna and in Aire sur l'Adour 1999 (Engel et al., 1999).

3.2 Results for the Flight on 14 November 1996

For the León flight, no measurements of long-lived tracers from the cryogenic whole air sampler on board the TRIPLE payload are available because of problems with the sealing of the air samples. Thus no measurements of either CH₄ or N₂O and no information about the total amount of inorganic chlorine Cl_y are available. Therefore to initialize the model simulations we use measurements of the Halogen Occultation Experiment (HALOE) on board the UARS satellite (Russell et al., 1993) and tracer-tracer correlations.

For November 1996, HALOE measurements are available in northern hemisphere midlatitudes within 35° N–50° N for the time period of 1–5 November and of 15–22 November. Thus for 14 November, the day of the TRIPLE flight, no

HALOE observations exist in the in northern hemisphere midlatitudes. Performing a potential vorticity (PV) analysis of the HALOE measurements shows that the HALOE measurements were conducted both within and outside of the polar vortex depending on longitude due to the distinct asymmetric form of the vortex that was shifted away from the North Pole. From meteorological analysis the air masses probed during the TRIPLE flight were led around the polar vortex before the measurement (cf. Sect. 2.1). Therefore we derived two data sets to initialize the model simulations; one for midlatitude air masses (case 1) and one for polar air masses (case 2). The following PV criterion was used to separate midlatitude and polar air masses:

Table 2. Mixing ratios of the major chemical species used to initialize the model simulations for the flight on 5 May 1999 launched in Aire sur l’Adour for the 9th cycle.

THETA [K]	600	600	700	700	800	800	850	850	866	886	875	874	874	871	871
trajno ^a	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15
SZA ^{b,o}	91.8	70.5	90.4	73.2	88.8	76.3	88.0	79.0	80.0	82.0	83.0	84.0	84.8	86.1	87.0
CH ₄ , ppmv	1.29	1.29	1.01	1.01	0.78	0.78	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68
Cl _y , ppbv	2.11	2.11	2.88	2.88	3.20	3.20	3.32	3.32	3.32	3.32	3.32	3.32	3.32	3.32	3.32
HCl, ppbv	1.16	1.16	1.56	1.56	1.87	1.87	2.01	2.01	2.01	2.01	2.01	2.01	2.01	2.01	2.01
CIO, pptv	3.58	81.33	18.53	129.44	45.88	167.85	63.78	171.96	170.10	156.27	137.37	124.49	113.27	93.88	82.48
ClONO ₂ , ppbv	0.94	0.86	1.29	1.18	1.28	1.16	1.23	1.13	1.13	1.14	1.16	1.17	1.18	1.20	1.21
NO _y , ppbv	7.17	7.17	12.40	12.40	16.05	16.05	16.76	16.76	16.76	16.76	16.76	16.76	16.76	16.76	16.76
NO, ppbv	0.27	0.86	1.34	1.92	2.22	2.66	2.59	2.95	2.97	2.96	2.91	2.88	2.86	2.77	2.72
NO ₂ , ppbv	1.64	1.05	2.82	2.23	3.30	2.86	3.46	3.11	3.09	3.09	3.14	3.17	3.19	3.28	3.34
HNO ₃ , ppbv	3.12	3.37	4.41	4.82	5.04	5.56	4.46	4.85	4.61	4.25	4.34	4.31	4.28	4.26	4.21
N ₂ O ₅ , ppbv	0.48	0.39	1.15	1.00	2.00	1.80	2.41	2.27	2.39	2.57	2.51	2.52	2.53	2.54	2.55
O ₃ ^c , ppmv	4.46	4.46	5.61	5.61	6.36	6.36	6.82	6.82	6.82	6.82	6.82	6.82	6.82	6.82	6.82
H ₂ O, ppmv	4.75	4.75	5.36	5.36	5.63	5.63	5.70	5.70	5.70	5.70	5.70	5.70	5.70	5.70	5.70
CO, ppbv	16.91	16.92	18.90	18.88	20.68	20.59	21.42	21.40	21.86	22.49	22.15	22.12	22.12	22.04	22.06
A _{SSA} ^d , μm ² cm ^{−3}	0.61	0.61	0.42	0.42	0.31	0.31	0.27	0.27	0.26	0.25	0.25	0.25	0.25	0.26	0.26
temperature ^b , K	215.53	215.53	220.78	220.81	226.97	226.91	230.09	230.16	231.22	232.50	231.79	231.70	231.69	231.50	231.55
pressure ^b , hPa	28.15	28.21	17.89	17.92	12.26	12.32	10.43	10.39	9.94	9.40	9.70	9.73	9.74	9.82	9.80
altitude ^b , km	24.99	24.98	28.17	28.15	30.81	30.78	31.94	31.97	32.27	32.67	32.45	32.42	32.42	32.36	32.38

^a Trajectory number
^b Values at the end of the trajectory
^c Initial mixing ratios for all cycles
^d Surface area of the background aerosol per unit volume

Table 3. Mixing ratios of the major chemical species used to initialize the model simulations for the flight on 14 November 1996 launched in León for midlatitude air masses (case 1) and for the 9th cycle.

THETA [K]	500	500	600	600	650	650	700	750	800	800	850	850	900	900
trajno ^a	01	02	03	04	05	06	07	08	09	10	11	12	13	14
SZA ^{b,o}	87.1	64.2	84.9	66.4	83.8	67.6	83.1	82.4	81.5	71.0	79.4	73.3	76.0	74.9
CH ₄ , ppmv	1.29	1.29	1.14	1.14	1.14	1.14	1.13	1.11	1.09	1.09	1.02	1.02	0.97	0.97
Cl _y , ppbv	1.80	1.80	2.53	2.53	2.57	2.57	2.60	2.67	2.78	2.78	2.97	2.97	3.10	3.10
HCl, ppbv	1.24	1.24	1.54	1.54	1.63	1.63	1.77	1.95	2.11	2.11	2.27	2.27	2.40	2.40
CIO, pptv	10.35	57.33	39.76	115.38	49.49	117.40	53.27	57.00	66.26	122.16	94.34	138.14	140.00	148.65
ClONO ₂ , ppbv	0.55	0.50	0.95	0.86	0.88	0.80	0.77	0.66	0.59	0.53	0.60	0.56	0.56	0.55
NO _y , ppbv	6.42	6.42	10.15	10.15	10.40	10.40	10.61	11.09	11.90	11.90	13.52	13.52	14.79	14.79
NO, ppbv	0.24	0.32	0.74	0.84	1.30	1.42	2.21	3.44	5.08	5.31	6.81	6.97	8.45	8.48
NO ₂ , ppbv	0.38	0.30	1.01	0.91	1.56	1.43	2.32	3.13	3.95	3.72	4.69	4.53	5.11	5.09
HNO ₃ , ppbv	4.79	4.97	6.11	6.58	4.87	5.40	3.13	1.64	0.63	0.80	0.30	0.35	0.11	0.12
N ₂ O ₅ , ppbv	0.18	0.11	0.59	0.40	0.82	0.59	1.03	1.06	0.80	0.74	0.55	0.54	0.27	0.28
O ₃ ^c , ppmv	2.12	2.12	4.54	4.54	5.44	5.44	6.00	6.41	6.66	6.66	6.79	6.79	6.78	6.78
H ₂ O, ppmv	4.35	4.35	4.79	4.79	4.84	4.84	4.88	4.90	4.91	4.91	4.95	4.95	5.06	5.06
CO, ppbv	23.35	23.31	23.14	23.07	23.01	22.93	22.92	22.92	23.01	22.94	23.20	23.18	23.49	23.49
A _{SSA} ^d , μm ² cm ^{−3}	0.95	0.95	0.61	0.60	0.49	0.50	0.41	0.35	0.30	0.30	0.26	0.26	0.23	0.23
temperature ^b , K	211.21	210.57	212.33	211.84	213.39	213.11	215.09	216.78	218.56	218.35	220.91	220.94	224.05	224.00
pressure ^b , hPa	49.20	48.60	26.77	26.39	20.35	20.50	16.16	13.09	10.63	10.70	9.09	9.01	7.71	7.72
altitude ^b , km	21.08	21.17	25.34	25.44	27.26	27.21	28.88	30.35	31.81	31.77	32.91	32.97	34.05	34.05

^a Trajectory number
^b Values at the end of the trajectory
^c Initial mixing ratios for all cycles
^d Surface area of the background aerosol per unit volume

Midlatitude			
Θ	600 K	700 K	900 K
PV	< 70 PVU	< 120 PVU	< 400 PVU
Vortex			
Θ	600 K	700 K	800 K
PV	> 80 PVU	> 150 PVU	> 300 PVU

The PV criterion was determined by analyzing the PV – CH₄ and the O₃ – CH₄ correlations observed by HALOE.

For both midlatitude and vortex conditions, simulations and measured CIO mixing ratio show a good agreement during float and night-time. During daylight, simulations are at the lower limit of the uncertainties of the CIO measurements and significantly underestimate the measurements at around

Table 4. Mixing ratios of the major chemical species used to initialize the model simulations for the flight on 14 November 1996 launched in León for vortex air masses (case 2) and for the 9th cycle.

THETA [K]	500	500	600	600	650	650	700	750	800	800	850	850	900	900
trajno ^a	01	02	03	04	05	06	07	08	09	10	11	12	13	14
SZA ^b	87.1	64.2	84.9	66.4	83.8	67.6	83.1	82.4	81.5	71.0	79.4	73.3	76.0	74.9
CH ₄ , ppmv	1.19	1.19	0.95	0.95	0.84	0.84	0.73	0.64	0.58	0.58	0.55	0.55	0.52	0.52
Cl ₂ , ppbv	2.34	2.34	2.96	2.96	3.14	3.14	3.26	3.31	3.33	3.33	3.33	3.33	3.33	3.33
HCl, ppbv	1.48	1.48	1.97	1.97	2.16	2.16	2.33	2.45	2.51	2.51	2.53	2.53	2.55	2.55
CIO, pptv	16.64	89.39	34.53	94.51	42.93	95.69	51.01	61.32	77.33	143.44	106.30	156.78	158.24	168.14
CIONO ₂ , ppbv	0.84	0.76	0.94	0.88	0.94	0.88	0.87	0.80	0.73	0.66	0.69	0.63	0.62	0.61
NO _y , ppbv	9.01	9.01	13.37	13.37	15.19	15.18	16.42	16.72	16.25	16.25	15.99	15.99	15.69	15.69
NO, ppbv	0.16	0.22	1.08	1.23	2.35	2.56	3.81	5.17	6.24	6.40	7.01	7.11	7.66	7.68
NO ₂ , ppbv	0.32	0.26	1.31	1.17	2.22	2.02	3.01	3.58	3.89	3.72	4.10	4.00	4.20	4.18
HNO ₃ , ppbv	7.19	7.42	8.42	8.94	7.46	8.07	6.08	4.33	2.67	3.14	1.68	1.92	1.03	1.06
N ₂ O ₅ , ppbv	0.19	0.11	0.74	0.50	1.05	0.77	1.27	1.38	1.33	1.12	1.23	1.14	1.07	1.06
O ₃ ^c , ppmv	2.50	2.50	4.03	4.03	4.21	4.21	4.39	4.67	5.07	5.07	5.43	5.43	5.74	5.74
H ₂ O, ppm	4.74	4.74	5.34	5.34	5.59	5.59	5.86	6.10	6.25	6.25	6.26	6.26	6.25	6.25
CO, ppb	23.30	23.24	23.10	23.02	22.95	22.87	22.67	22.35	22.03	21.86	21.88	21.77	21.87	21.85
ASSA ^d , $\mu\text{m}^2\text{cm}^{-3}$	0.96	0.96	0.61	0.61	0.50	0.50	0.41	0.35	0.30	0.30	0.26	0.26	0.23	0.23
temperature ^b , K	211.21	210.57	212.33	211.84	213.39	213.11	215.09	216.78	218.56	218.35	220.91	220.94	224.05	224.00
pressure ^b , hPa	49.20	48.60	26.77	26.39	20.35	20.50	16.16	13.09	10.63	10.70	9.09	9.01	7.71	7.72
altitude ^b , km	21.08	21.17	25.34	25.44	27.26	27.21	28.88	30.35	31.81	31.77	32.91	32.97	34.05	34.05

^a Trajectory number^b Values at the end of the trajectory^c Initial mixing ratios for all cycles^d Surface area of the background aerosol per unit volume**Table 5.** Simulated CIO mixing ratios (end of trajectory) for the 9th cycle for different model input of surface areas of the background aerosol per unit volume ASSA.

Aire sur l'Adour 1999														
THETA [K]	600	600	700	700	800	800	850	850	866	886	875	874	874	871
ASSA ^a , $\mu\text{m}^2\text{cm}^{-3}$	0.61	0.61	0.42	0.42	0.31	0.31	0.27	0.27	0.26	0.25	0.25	0.25	0.25	0.26
CIO ^b , pptv	3.45	78.00	17.57	122.32	41.99	153.44	57.43	154.32	149.38	133.22	119.15	108.21	98.51	82.02
ASSA ^b , $\mu\text{m}^2\text{cm}^{-3}$	1.13	1.13	0.78	0.78	0.57	0.57	0.50	0.50	0.48	0.46	0.47	0.47	0.47	0.47
CIO ^b , pptv	3.50	79.96	17.73	124.16	42.30	154.79	57.82	155.41	150.39	134.07	119.93	108.92	99.16	82.57
ASSA ^c , $\mu\text{m}^2\text{cm}^{-3}$	0.24	0.24	0.17	0.17	0.12	0.12	0.11	0.11	0.10	0.10	0.10	0.10	0.10	0.10
CIO ^c , pptv	3.40	76.19	17.44	120.74	41.74	152.33	57.12	153.45	148.58	132.54	118.52	107.65	97.99	81.59
León 1996 case 1 (midlat)														
THETA [K]	500	500	600	600	650	650	700	750	800	800	850	850	900	900
ASSA ^a , $\mu\text{m}^2\text{cm}^{-3}$	0.95	0.95	0.61	0.60	0.49	0.50	0.41	0.35	0.30	0.30	0.26	0.26	0.23	0.23
CIO ^b , pptv	10.04	55.11	39.13	113.17	48.70	115.32	52.35	55.93	64.25	118.54	89.01	130.02	126.86	134.71
ASSA ^b , $\mu\text{m}^2\text{cm}^{-3}$	1.76	1.76	1.12	1.11	0.91	0.92	0.76	0.64	0.55	0.55	0.48	0.48	0.42	0.42
CIO ^b , pptv	10.35	57.56	40.12	117.13	49.70	118.42	53.17	56.50	64.54	119.23	89.19	130.35	126.97	134.84
ASSA ^c , $\mu\text{m}^2\text{cm}^{-3}$	0.38	0.38	0.24	0.24	0.20	0.20	0.16	0.14	0.12	0.12	0.10	0.10	0.09	0.09
CIO ^c , pptv	9.65	52.26	37.99	108.96	47.62	112.13	51.52	55.39	64.00	117.94	88.86	129.76	126.77	134.61
León 1996 case 2 (vortex)														
THETA [K]	500	500	600	600	650	650	700	750	800	800	850	850	900	900
ASSA ^a , $\mu\text{m}^2\text{cm}^{-3}$	0.96	0.96	0.61	0.61	0.50	0.50	0.41	0.35	0.30	0.30	0.26	0.26	0.23	0.23
CIO ^b , pptv	16.35	87.42	34.11	93.13	42.18	93.80	50.10	60.58	76.69	142.78	104.95	154.99	153.87	163.61
ASSA ^b , $\mu\text{m}^2\text{cm}^{-3}$	1.77	1.77	1.13	1.12	0.92	0.92	0.76	0.65	0.55	0.55	0.49	0.48	0.42	0.42
CIO ^b , pptv	16.84	91.35	35.06	96.44	43.07	96.21	50.88	61.28	77.30	144.02	105.57	155.91	154.47	164.25
ASSA ^c , $\mu\text{m}^2\text{cm}^{-3}$	0.38	0.38	0.24	0.24	0.20	0.20	0.16	0.14	0.12	0.12	0.10	0.10	0.09	0.09
CIO ^c , pptv	15.70	82.74	33.03	89.64	41.24	91.37	49.33	59.91	76.12	141.65	104.41	154.18	153.36	163.07

^a Standard simulation^b Simulation with higher ASSA values^c Simulation with lower ASSA values

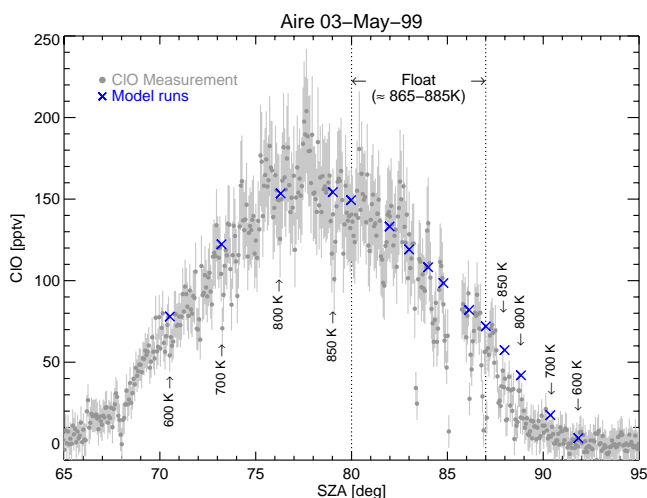


Fig. 6. Simulated ClO mixing ratios as a function of SZA compared to measured ClO mixing ratios of the TRIPLE flight launched on 3 May 1999 in Aire sur l'Adour. The uncertainties of the ClO measurements are shown as gray bars (1σ accuracy, see Fig. 3). The chemistry along each 24-hour backward trajectory is calculated a few times using the results of the previous model simulation to initialize the following simulation. Here model simulations are shown after 9 such cycles. For details concerning the model scenario see text. The corresponding levels of potential temperature are labeled by arrows.

650 K potential temperature during the most sunlit portion of the flight (SZA about 67°). Only at 500 K does case 1 reproduce the ClO daylight measurements. In general, the simulations for midlatitude conditions are somewhat lower than for vortex conditions above 700 K and somewhat higher below, except at 500 K (see Fig. 8). We note that although the Cl_y values are for vortex conditions higher than for midlatitude conditions, simulated ClO mixing ratios for case 2 are less than for case 1 between 600 and 700 K. Presumably, this difference is driven by higher NO_x mixing ratios for vortex conditions. For both cases, the maximum of the distribution is shifted to larger SZAs compared to the measurements. The simulated diurnal variation of ClO and various other species for different levels of potential temperature are shown in Fig. 9. The sensitivity of the model simulations toward A_{SSA} was also examined in the same way as for the flight launched in Aire sur l'Adour (cf. Table 5). For both cases, the sensitivity of ClO mixing ratios on A_{SSA} values is $<6\%$ below 700 K and $<2\%$ above.

3.2.1 Discrepancy for daylight ClO at around 650 K

Here we discuss possible reasons for the discrepancy between simulations and measurements for the ClO daylight profile at around 650 K. At midlatitudes, chlorine nitrate is formed by the reaction of ClO with NO_2 and is dissociated by photolysis in the ultraviolet (e.g., Brasseur and Solomon, 1984):

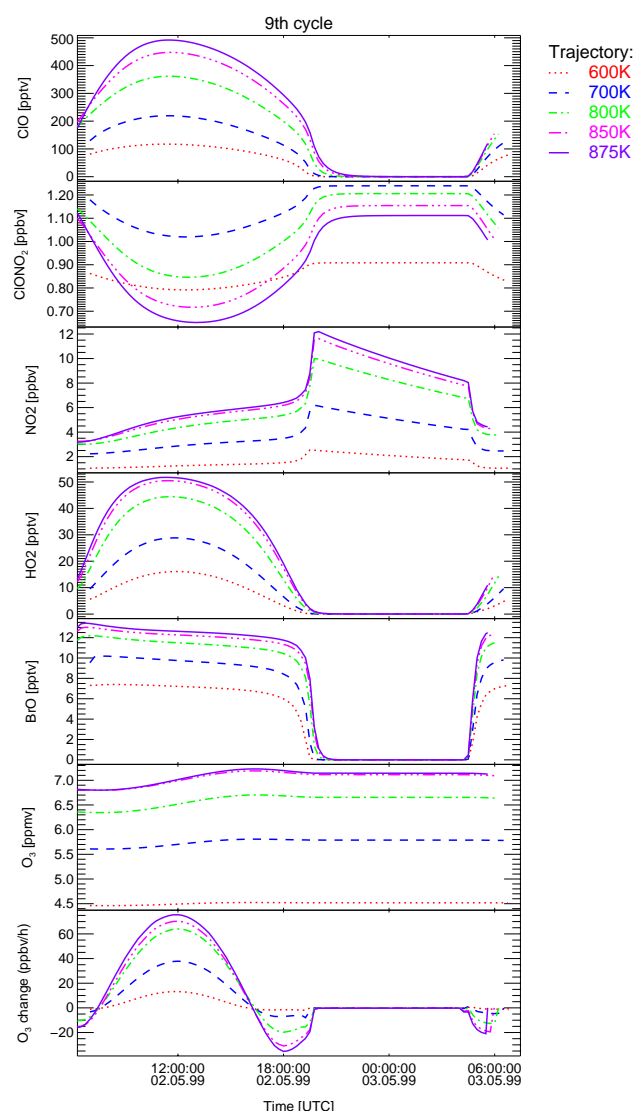
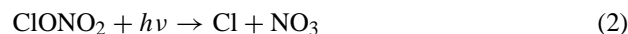
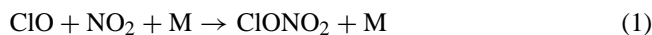


Fig. 7. For the flight launched on 3 May 1999 in Aire sur l'Adour, the simulated diurnal variation of ClO, ClONO_2 , NO_2 , HO_2 , BrO, O_3 mixing ratios, and the rate of ozone change in ppbv per hour are shown between 600 K and 875 K potential temperature for the 9th cycle.



Thus the concentration of daylight ClO depends on the concentration of night-time ClONO_2 . Therefore underestimated ClO mixing ratios would imply that ClONO_2 is underestimated and thus HCl is overestimated by the model. Simulations initialized with HCl mixing ratios reduced by about 20% (equivalent to approximately the minimum HCl mixing ratios measured by HALOE) and using the same Cl_y

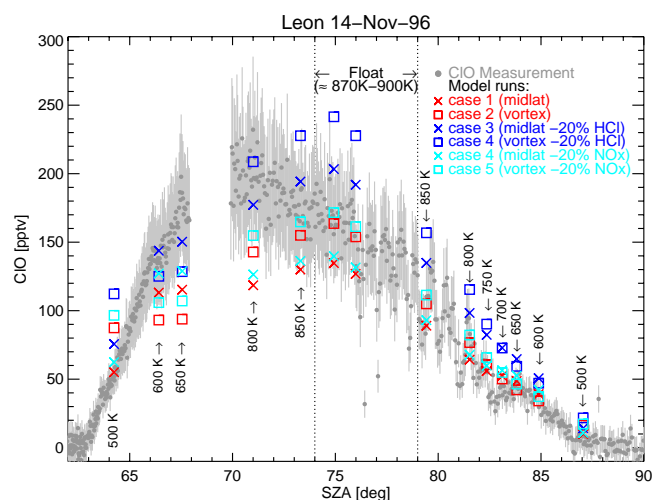


Fig. 8. Simulated ClO mixing ratios as a function of SZA compared to measured ClO mixing ratios of the TRIPLE flight launched on 14 November 1996 in León. The uncertainties of the ClO measurements are shown as gray bars (1σ accuracy, see Fig. 3). The chemistry along each 24-hour backward trajectory is calculated a few times using the results of the previous model simulation to initialize the following simulation. Here model simulations are shown after 9 such cycles. For case 1 and 2 the model is initialized using a data set representing midlatitude air masses and vortex air masses, respectively (cf. Sect. 3.2). For details concerning the different model scenarios see text. The corresponding levels of potential temperature are labeled by arrows.

as in case 1 or case 2 reproduce the ClO daylight measurements after 9 cycles, but significantly overestimate the ClO night-time measurements after 9 cycles for both midlatitude and vortex conditions (see case 3 and 4, Fig. 8).

Further in the lower stratosphere, ClO is inversely correlated with NO_2 (Stimpfle et al., 1994). In a sensitivity study, the initial NO_x mixing ratios were reduced by about 20% (equivalent to approximately the minimum NO_x mixing ratios measured by HALOE), where the same NO_y was used as in case 1 and 2 (see case 5 and 6, Fig. 8). Nonetheless, the measured ClO daylight values are still underestimated or are at the lower limit of the uncertainty of the ClO measurements by the simulations after 9 cycles and simultaneously the measured ClO night-time values are at the upper limit of the measurements.

In summary, uncertainties in the initialization of HCl and NO_x might cause the discrepancies in the ClO daylight profile at around 650 K. However, no initialization could be derived so that model simulations simultaneously reproduced the entire measured ClO daylight and night-time profile. Nevertheless, the comparison between ClO measurements and simulations (see Fig. 8) is consistent with the view that vortex air masses are probed above 650 K and air masses originating from midlatitudes are probed below 650 K, because for these cases simulated ClO mixing ratios simul-

taneously agree with the measurements for night-time and daylight conditions. These findings are confirmed by calculations of 10-day backward trajectories using ERA-40 Re-Analyses wind data produced by ECMWF (European Centre for Medium-Range Weather Forecasts) (see Fig. 10). The comparison between simulations and measurements indicates that at 650 K potential temperature, vortex air masses are probed during ascent and midlatitude air masses are detected during descent. In calculations of 10-day backward trajectories using wind data from both the UK Met Office (UKMO) analyses and ERA-40 Re-Analyses the origin of the air masses sampled during the balloon ascent and descent are located relatively close together (see Fig. 10). But it also may be expected that 10-day backward trajectories using wind data with a time resolution of 24 h and 6 h, respectively, cannot precisely resolve the origin of air masses probed between ascent and descent which differ within a time interval of approximately 2–3 h.

Nevertheless, we analyzed further reasons independent of the initialization of the model simulations and the dynamic conditions of the flight that could explain the uncertainties for the León flight, although the simulations of the Aire sur l'Adour flight show an excellent agreement with the measurements and thus indicate that no substantial uncertainties exist in midlatitude chlorine chemistry. The quantum yields of the two ClONO_2 photolysis channels ($\text{ClONO}_2 + h\nu \rightarrow \text{ClO} + \text{NO}_2$ and $\text{ClONO}_2 + h\nu \rightarrow \text{Cl} + \text{NO}_3$) are taken from standard recommendations (Sander et al., 2002). Nickolaissen et al. (1996) observed Cl pressure dependence of the quantum yield for the ClONO_2 photolysis beyond 300 nm. If model simulations do not consider the effect of pressure on the ClONO_2 photolysis, models would tend to over-predict HCl and under-predict ClONO_2 and thus ClO mixing ratios in the lower stratosphere. In our study, in order to reproduce ClO mixing ratios measured during daylight by model simulations, J_{ClONO_2} would have to be increased by a factor of two or more (for case 1 and 2). In this case, the measured ClO night-time and float profiles would be substantially overestimated by model simulations. Thus it is unlikely that uncertainties in J_{ClONO_2} are the major source of the discrepancies between measurements and simulations in the ClO daylight profile. Furthermore, the quantum yield for the ClONO_2 photolysis channels beyond 300 nm was modified in the model simulations. Even by neglecting the $\text{Cl} + \text{NO}_3$ channel in favor of the $\text{ClO} + \text{NO}_2$ channel beyond 300 nm, no evidence is found here that a significant change in the quantum yield has any influence on ClO mixing ratios.

Avallone et al. (1993) found in a comparison of ClO in situ balloon measurements and model simulations a good agreement, except below 20 km altitude, where observed ClO is higher than simulated ClO by as much as a factor of four. A mechanism responsible for maintaining these high ClO mixing ratios was at that time unclear, whereas reaction rates and absorption cross-sections were taken from DeMore et al. (1992). In our study, we found no discrepancies below

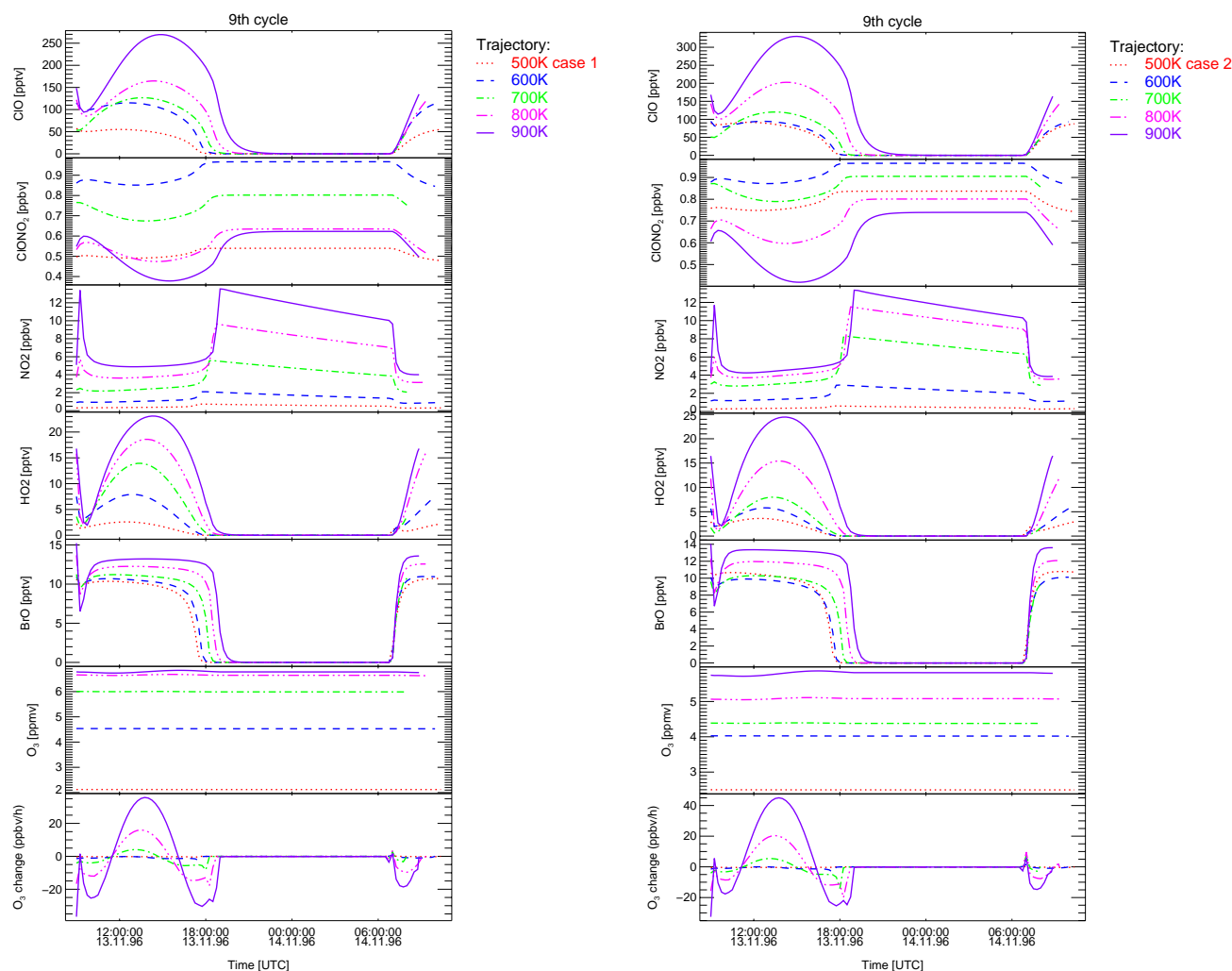


Fig. 9. For the flight launched on 14 November 1996 in León, the simulated diurnal variation for case 1 (left panel) and case 2 (right panel) of CIO, ClONO_2 , NO_2 , HO_2 , BrO , O_3 mixing ratios, and the rate of ozone change in ppbv per hour are shown between 500 K and 900 K potential temperature for the 9th cycle.

20 km altitude between measured and simulated CIO mixing ratios using reaction rate constants and absorption cross-sections from current standard recommendations (Sander et al., 2002).

3.3 SZA Dependence of Simulated CIO to Measured CIO

The deviation of simulated CIO ($\text{CIO}^{\text{Model}}$) from measured CIO (CIO^{Meas}) is analyzed as a function of the SZA. For this purpose, the measured CIO mixing ratios were averaged in SZA intervals of 0.5° . The average properties of these SZA intervals are shown in Table 6. To take into account the uncertainties of the model simulations we calculate the ratio $\text{CIO}^{\text{Model}}/\text{CIO}^{\text{Meas}}$ (R_{CIO}) for each model trajectory and for all sensitivity simulations shown in Figs. 6 and 8. A ten-

dency of R_{CIO} to increase for SZAs larger than 87° is found for the Aire flight (see Fig. 11). For the León flight, we have no R_{CIO} values for SZAs larger than 87° . However, for measurements at 87° , R_{CIO} is also increased, in contrast to R_{CIO} at 87° for the Aire flight. All other R_{CIO} values are in the interval $1.0+0.32/-0.03$ for the Aire sur l'Adour flight and in the interval $1.0+1.10/-0.45$ for the León flight including the discrepancy found in the CIO daylight profile at around 650 K.

Clearly for SZA larger than 86° – 87° the model substantially overestimates the observed CIO mixing ratios. The reason for this discrepancy is not known at present. Further evidence exists indicating that for high solar zenith angles the stratospheric chlorine chemistry is not completely understood. Rivière et al. (2003) reported that the comparison of

Table 6. Average properties of the SZA intervals for the ClO measurements as shown in Fig. 11.

trajno	SZA ^a	N ^b	$\overline{\text{ClO}}$ [pptv] ^c	$S(\overline{\text{ClO}})$ [pptv] ^d	rel. $S(\overline{\text{ClO}})$ [%]	press [hPa]	alt [km]
Aire sur l'Adour 1999							
1.0	91.8	18.0	0.3	0.9	313.3	27.5	24.2
2.0	70.5	17.0	68.7	2.1	3.1	27.5	24.3
3.0	90.4	18.0	6.6	1.4	20.9	17.6	27.1
4.0	73.2	16.0	113.8	4.0	3.5	17.7	27.0
5.0	88.8	18.0	16.5	2.3	13.7	11.8	29.5
6.0	76.3	16.0	157.7	3.8	2.4	12.5	29.3
7.0	88.0	18.0	34.0	3.3	9.8	10.0	30.5
8.0	79.0	17.0	147.9	4.5	3.1	10.5	30.4
9.0	80.0	17.0	140.9	3.5	2.5	9.9	30.5
10.0	82.0	17.0	126.1	3.8	3.0	9.7	30.7
11.0	83.0	17.0	113.4	9.1	8.1	9.5	31.1
12.0	84.0	17.0	96.7	5.1	5.3	9.4	31.1
13.0	84.8	14.0	74.8	7.3	9.7	9.3	31.0
14.0	86.1	16.0	72.4	4.4	6.1	9.3	31.1
15.0	87.0	18.0	58.1	5.2	8.9	9.3	31.1
León 1996							
1.0	87.1	18.0	4.3	1.1	24.2	50.0	20.9
2.0	64.2	36.0	53.4	2.0	3.7	47.9	20.8
3.0	84.9	18.0	33.5	1.8	5.3	27.5	24.4
4.0	66.4	30.0	140.3	1.2	0.9	26.7	24.0
5.0	83.8	18.0	42.3	1.1	2.7	20.4	26.4
6.0	67.6	26.0	170.7	2.2	1.3	19.6	26.2
7.0	83.1	18.0	39.7	1.4	3.6	16.4	27.8
8.0	82.4	18.0	47.9	2.7	5.6	13.5	28.8
9.0	81.5	18.0	65.7	3.9	5.9	11.2	30.2
10.0	71.0	23.0	201.1	2.8	1.4	11.4	29.5
11.0	79.4	19.0	107.4	4.5	4.2	9.2	31.2
12.0	73.3	21.0	172.9	2.4	1.4	9.3	30.7
13.0	76.0	19.0	141.7	8.1	5.7	8.8	33.5
14.0	74.9	19.0	166.2	3.1	1.8	8.9	35.0

^a Center of the SZA bins of $\pm 0.25^\circ$ ^b Number of elements within bin^c Average ClO mixing ratio within bin^d Standard deviation of the mean:
$$S(\overline{\text{ClO}}) = \sqrt{\frac{1}{N(N-1)} \sum_{i=1}^N (\overline{\text{ClO}} - \text{ClO}_i)^2}$$

The absolute error of $\overline{\text{ClO}}$ is (20–23%), even if $S(\overline{\text{ClO}})$ is lower due to statistics.

night-time balloon-borne measurements of OCIO and NO₂ in the Arctic polar vortex with model simulations shows that some uncertainties still exist in the interaction between nitrogen and halogen species.

4 Summary and Conclusions

We have presented two balloon-borne in situ measurements of ClO conducted in late fall and late spring in the northern hemisphere midlatitudes stratosphere during the period of maximum total inorganic chlorine in the atmosphere. Both ClO measurements were conducted on board the TRIPLE balloon payload launched in November 1996 in León, Spain,

and in May 1999 in Aire sur l'Adour, France. For both flights a vertical ClO daylight and night profile were obtained over an altitude range of approximately 15–35 km.

Using the photochemical box model version of the CLaMS model (McKenna et al., 2002a,b) simulations along 24-hour backward trajectories were presented to study the diurnal variation of ClO in the lower midlatitude stratosphere. The simulations were initialized with all available stratospheric measurements, together with tracer-tracer correlations, and information deduced from a 2-D model. The flight launched in León is characterized by a more complex dynamical situation (possible contribution of a mix of vortex and non-vortex air) and fewer constraints for the model calculations

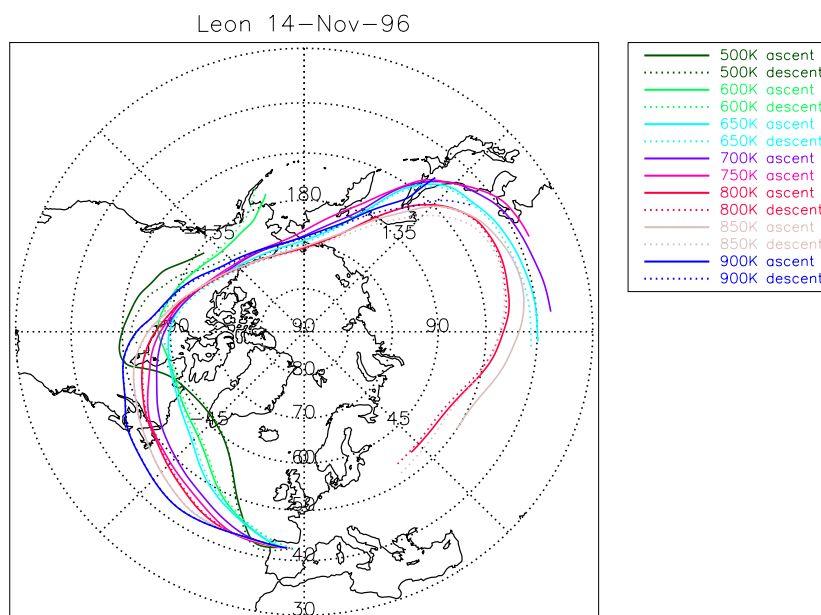


Fig. 10. Calculations of 10-day backward trajectories using ERA-40 Re-Analyses wind data produced by ECMWF (European Centre for Medium-Range Weather Forecasts) for the flight launched on 14 November 1996 in León.

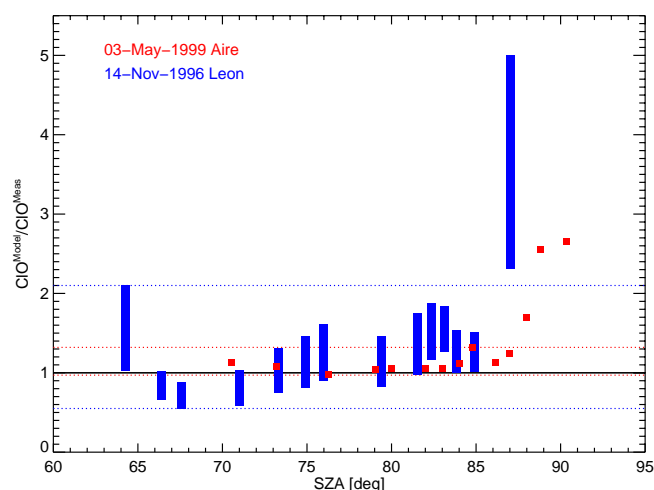


Fig. 11. The ratio of simulated to measured CIO mixing ratios as a function of SZA. The measured CIO mixing ratios are averaged in SZA intervals of 0.5° centered at the SZA endpoint of each trajectory (cf. Table 6). The ratio $\text{CIO}^{\text{Model}}/\text{CIO}^{\text{Meas}}$ is calculated for each model trajectory and for all sensitivity simulations shown in Figs. 6 and 8. The relative measurement error of CIO^{Meas} ($=\text{CIO}$) for 92° SZA for the flight launched in León is very large (cf. Table 6) and is not shown here. All the ratios $\text{CIO}^{\text{Model}}/\text{CIO}^{\text{Meas}}$ are in the interval $1.0 \pm 0.32 / -0.03$ for the Aire sur l'Adour flight (red dotted line) and in the interval $1.0 \pm 1.10 / -0.45$ for the León flight (blue dotted line), except for SZAs larger than 86° – 87° .

available from tracer measurements in contrast to the flight launched in Aire sur l'Adour. For the flight launched in Aire sur l'Adour 1999, the model simulations show a very good

agreement with the CIO measurements over the entire altitude range of 20–35 km and for both the daylight and nighttime profile. The present results show that simulated CIO mixing ratios likewise reproduce the measured CIO mixing ratios for the flight launched in León. A tendency that simulated CIO mixing ratios overestimate measured CIO mixing ratios for SZAs larger than 86° – 87° is consistently found for both flights. In summary, we conclude that for SZAs lower than 86° no indication can be deduced from the present CIO measurements that substantial uncertainties exist in midlatitude chlorine chemistry of the stratosphere. For SZAs larger than 86° – 87° further studies are required.

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